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THE EVOLUTION OF LIMESTONE AND DOLOMITE. I

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INTRODUCTION

Many writers[1] have called attention to the decrease in the percentage of dolomite in going up the geologic time scale, and

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[1] Daly has shown the decrease in dolomite with age in the following compilation of analyses (Table I, from *Bull. Geol. Soc. Am.*, XX, 165):

TABLE I

AVERAGE RATIO OF CALCIUM TO MAGNESIUM IN LIMESTONES OF DIFFERENT PERIODS

Period	1 Number of Analyses	2 Ratio of $CaCO_3$ to $MgCO_3$	3 Ratio of Ca to Mg
Pre-Cambrian:			
a) From North America, except those in b)	28	1.64:1	2.30:1
b) From Ontario (Miller)	33	4.92:1	6.89:1
c) Average of a) and b)	61	2:93:1	4.10:1
d) Best general average	49	2.58:1	3.61:1
Cambrian (including 17 of the Shenandoah limestone)	30	2.96:1	4.14:1
Ordovician	93	2.72:1	3.81:1
Silurian	208	2.09:1	2.93:1
All pre-Devonian	392	2.39:1	3.35:1
Devonian	106	4.49:1	6.29:1
Carboniferous	238	8.89:1	12.45:1
Cretaceous	77	40.23:1	56.32:1
Tertiary	26	37.92:1	53.09:1
Quaternary and Recent	26	25.00:1	35.00:1
Total	865		

various hypotheses have been offered for its explanation. Probably the majority of geologists hold that it is due to a secondary alteration of limestone to dolomite, which is roughly proportional to time. Daly[1] has suggested that it is due to a change in the nature of the life processes which effect the precipitation of carbonates in the sea. Still another alternative hypothesis is herewith offered, that the percentage of dolomite developed in the sea has declined with time, and that this was controlled by a progressive increase in the ratio of calcium to magnesium contributed from the lands.

Absolute proof for any one of these hypotheses is impossible from the very nature of the problem. For instance, all of them are based on the theory of uniformitarianism, a theory deep rooted in geologic evidence, but a theory nevertheless. All the hypotheses offered involve the question of whether dolomite develops predominantly in the sea, regardless of the specific processes of formation, or whether it is predominantly a secondary product from limestones, after their emergence from the sea. If its origin is mainly in the sea, which of the factors controlling deposition in the sea has changed so as to cause a decline in its deposition with time? Was it temperature, pressure, life processes, the chemical composition of the sea, or some combination of these factors? To these no final answer can be made. The available evidence for each view can be sifted. Conclusions may be drawn, but the probability may be freely recognized that in the future some of the conclusions may become invalidated.

PART I. THE EVIDENCE ON THE ORIGIN OF DOLOMITE

That the predominance of dolomite in the ancient sediments is due in a larger measure to primary conditions of deposition in the sea than to the metamorphism of limestones after their emergence from the sea seems to follow from a comparison of the evidence on the origin of dolomite in the sea with that on the origin of dolomite by the metamorphism of limestone after its emergence from the sea.

A. THE EVIDENCE FOR THE ORIGIN OF DOLOMITE IN THE SEA

Interstratification of limestones, magnesian limestones, and dolomites the result of primary conditions of sedimentation, or of the

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[1] *Ibid.*

differential metamorphism of limestones after their emergence from the sea.—In a succession of conformable formations, each formation usually presents a certain specific lithologic unity of character which is different from that of adjacent formations, and may or may not be related to them by gradation phases. Thus limestones are not infrequently sharply interstratified with dolomites, and give by their color contrasts a graphic portrayal of the sharp lithologic difference which frequently distinguishes adjacent carbonate formations. Attention is directed to a number of typical illustrations of sharply defined stratigraphic cleavage between limestones and dolomites. The "lead and zinc" district of southwestern Wisconsin presents the following interesting succession:

System	Formation	Average Thickness in Feet	Lithological Character, etc.
Ordovician	Hudson River	160	Shale.
	Galena	250	Dolomite. Limestone layers, sharply interstratified near bottom.
	Containing oil rock	3±	Oily shale, not deposited everywhere.
	Clay	3±	Not deposited everywhere.
	Glassrock	3±	Sharply defined limestone. Very pure.
	Platteville	55	Magnesian limestone and dolomite.

A striking case of sharp interstratification of nearly pure limestone beds and dolomites is described by F. B. Peck[1] as occurring in the Trenton of Lehigh and Northhampton counties, Pa.

I. P. Lesley's[2] study of the Cambro-Silurian limestones of Cumberland County, Pennsylvania, is perhaps the most detailed quantitative chemical study of a limestone section which has ever been made from the viewpoint of throwing light on the origin of limestone and dolomite. The section studied was about 375 feet

[1] F. B. Peck, *Eco. Geol.*, III, No. 1, p. 43.

[2] I. P. Lesley, *Second Geol. Survey Pa.*, Vol. MM (1897), pp. 311–62.

thick, consisting of conformable, uniformly dense, slightly disturbed beds of limestone sharply interstratified with beds of magnesian limestone and dolomite. Analyses taken from various parts of each bed showed that each bed constituted a lithologic unit which often differed sharply from adjacent beds.

To E. Suess,[1] the sharply defined, thin-bedded intercalations of limestone and dolomite in the Plattenkalk present such powerful evidence of characters which could not have been acquired by metamorphism after their emergence from the sea, that he regards them as direct chemical precipitates. While it may be difficult to agree with Suess that chemical precipitation, in cases like that of the Plattenkalk, is proven, there certainly can be no doubt that it is easier to conceive of such formations as being the direct result of sedimentary processes in the sea, than to believe them to be the result of the differential metamorphism of limestone beds after their emergence from the sea. It is difficult to see how the metamorphism of a succession of conformable limestone beds or formations after their emergence from the sea could be so thoroughly selective as to result in a succession of beds or formations of unlike composition. Circulating underground water, the most universal agent of the alternation of sediments after their emergence from the sea, is obviously most effective along joints, bedding planes, or other large openings both parallel to and across the bedding, the so-called "trunk channels of circulation" repeatedly emphasized by Van Hise in his" Treatise on Metamorphism."

Until more direct evidence has been submitted for the origin of dolomite formations through circulating underground water, it seems more reasonable to assume that interstratifications of dolomite and limestone result from primary conditions of sedimentation, regardless of what the specific processes of limestone and dolomite building may have been.

Fineness of grain, peculiar to some dolomites, probably indicative of very little metamorphism since deposition.—Attention is directed to the fineness of grain which some dolomites possess. Daly[2] finds that the slightly disturbed dolomites of Cambrian and pre-Cambrian age of the forty-ninth parallel section of the Rocky Mountain geosynclinal, aggregating about 7,000 feet in thickness, are singularly monotonous in their fineness of grain, averaging about 0.02 millimeter. Other fine-grained and similarly undisturbed dolomites mentioned by Daly are those of the Archean at the headwaters of the Priest River, Idaho, the magnesian limestones and dolomites inclosing the chitinous fossil Beltina donai in the Clarke range and the Siyeh and Sheppard siliceous limestones of northwestern Montana, probably of middle Cambrian age. He also quotes Vogt as stating that the finest grained Norwegian dolomites average from 0.02 to 0.03 millimeter in diameter.

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[1] E. Suess, *The Face of the Earth*, II, 262.

[2] R. A. Daly, "The Evolution of the Limestones," *Bull. Geol. Soc. of America*, XX (1909), 167–68.

Willis and Blackwelder in their studies of the geology of China for the Carnegie Institution describe a number of very fine-grained, dense dolomites of considerable extent and thickness.

The pre-Cambrian dolomite formation of the Baraboo[1] synclinal is singularly fine grained. The Niagara limestone of Wisconsin, a dolomitic formation, is generally a very even-textured, fine-grained, and compact rock.

The generalization may be deduced from the facts cited that many undisturbed or only slightly disturbed dolomites are exceedingly fine grained and compact. There does not appear to be any evidence that this fineness of grain is the result of granulation. Furthermore, the relative mobility and regenerative power of the carbonates is very great as compared with the other minerals. Coarse-grained, even-textured[2] marbles showing no strain effects are found interbedded with banded gneisses with marked strain effects. Unless conditions are peculiarly unfavorable for recrystallization, the metamorphism of dolomites would probably result in coarser grain. The fineness of grain and compactness of many dolomites may therefore be interpreted as showing that they were dolomite before they emerged from the sea.

Many dolomite formations lack fossils.—The opinion is reflected from geologic literature that fossils are less common in dolomite than in limestone, although no quantitative study of this problem seems to have been made. It has been observed in various places that the limestone beds intercalated between dolomite are full of fossils, while the dolomite is barren. Illustrations of this are found in the Galena limestone of Wisconsin. The paucity of fossils in dolomites has been variously interpreted, some holding that fossils were never present in the formation because the conditions at the time of deposition were unfavorable to life, while others claim that they were originally present but have been destroyed by metamorphism. In connection with the first interpretation, it is interesting to note that magnesium-bearing solutions have actually been found to be unfavorable to life processes. It may be the correct interpretation in the case of certain dense, fine-grained dolomites. On the other hand, porous, cavernous dolomites like the Lower Magnesian of the Upper Mississippi valley, which is nearly devoid of fossils, evidently has undergone considerable recrystallization which may have destroyed the fossil record. No final conclusion seems to follow from the apparent fossil barrenness of dolomites with reference to the origin of dolomite.

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[1] S. Weidman, "Baraboo Iron-bearing District," *Wisconsin Survey Bull.*, No. 13 (1904), p. 67.

[2] C. R. Van Hise, "Treatise on Metamorphism," *U.S.G.S. Mon. 47*, p. 738.

Association of certain dolomites with gypsum and salt deposits.—Of certain dolomites which are found with deposits of salt, gypsum, and red beds and other indications of aridity and concentrated seas, it has been suggested that they are direct chemical precipitates, since conditions of deposition were apparently unfavorable to life. This view is open to the criticism that no case is known where this process is in operation at the present time. However, regardless of what the specific processes of dolomite building were, it seems more likely that these deposits were primarily dolomite because gypsum tends to decompose dolomite into calcium carbonate and magnesium sulphate. Therefore, if any alteration of the deposit had taken place since deposition, it would seem more likely to result in the decomposition of dolomite than in dolomitization.

Chemical precipitation of dolomite in the sea.—Crystals of dolomite grow in vugs and cavernous openings of coral reefs in the Pacific Ocean, according to E. W. Skeats.[1]

[1] E. W. Skeats, *Bull. Mus. Comp. Zoöl.*, XLII (1903), 53–126.

Experimental evidence for the chemical precipitation of dolomite.—The direct precipitation of dolomite from solution has apparently not been done, experimentally. Sterry Hunt[1] precipitated calcium carbonate and the hydrous carbonate of magnesium with sodium carbonate and found that he could develop dolomite by heating this mixture to 120° C.–130° C. Obviously this experiment did not accomplish direct chemical precipitation of dolomite nor is it applicable to the explanation of the majority of dolomites in nature.

Daly's hypothesis of the direct precipitation of dolomite in the primitive ocean.—Daly[2] postulates that dolomite was precipitated from a nearly limeless primitive ocean by ammonium carbonate generated by the decay of organisms on the bottom of the ocean. The hypothesis is based on several assumptions, namely: (*a*) the scavenging system of the pre-Cambrian and the early Paleozoic ocean was less perfect than at present; (*b*) the post-Huronian uplift gave a tremendous impetus to the transportation of lime to the sea, which in turn stimulated the development of lime-secreting organisms; (*c*) the improvement of the scavenging system and the development of lime-secreting organisms gradually brought the balance in favor of the deposition of limestones by organic secretions over direct chemical precipitation. The theory is offered to explain a number of facts: (*a*) the predominance of dolomite in the older formations; (*b*) characteristics such as grain, fossil record, and field relations of certain dolomites indicative of direct chemical precipitation; and (*c*) the apparent similarity between the ratio of calcium to magnesium in the older dolomites and the ratio of calcium to magnesium of streams on pre-Cambrian crystalline terranes. This theory fits many facts remarkably well. However, the premises on which it is based are open to objection.

It is true that the decay of marine organisms generates[3] ammonium carbonate and other precipitants. But organic decay also generates carbonic acid, which tends to keep the carbonates of lime and magnesia in solution. The rapid corrosion of marine shells is partly ascribed to this agency, by the authors of the Challenger deep-sea report. Thomson's[1] observations that the local abundance of carbonic acid on the ocean bottom is associated with an abundance of organisms is suggestive. Corrosion of calcareous remains by the direct action of sea water, but predominantly by the action of carbonic acid resulting from organic decay, is regarded by Murray as sufficiently powerful to prevent the accumulation of calcareous ooze at a mean depth of 2,730 fathoms, over 51,500,000 square miles of ocean bottom, the Red Clay area.

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[1] Sterry Hunt, *Chem. and Geol. Essays* (1895), 80.

[2] R. A. Daly, "First Calcareous Fossils and the Evolution of the Limestones," *Bull. Geol. Soc. of America*, XX, 153–70.

[3] G. Steinmann, *Ber. Naturforsch. Gesell. Freiburg*, IV (1889), 288; Challenger, *Report on Deep Seas*, 255.

It therefore seems to be an open question whether the net chemical effect resulting from organic decay in the ocean is precipitation or corrosion. The scavengers of the present ocean do not arrest the accumulation of calcareous oozes over millions of square miles of the ocean bottom. The evidence that direct precipitation of calcium carbonate is taking place on those vast areas of organic decay is doubtful. Philippi,[2] viewing direct chemical precipitation as an important process in the origin of limestones, after citing the data offered by various investigators for direct chemical precipitation from the present ocean, concludes that certain incrustations and the cements of some oozes are probably chemical precipitates. He believes that warm seas, teeming with life, where decay on the bottom is rapid are favorable localities for the precipitation of calcium carbonate.

The acquisition of the lime-secreting habit by marine organisms in response to an accumulation of lime in the ocean postulated as a result of the post-Huronian erosion cycle, and the increase in scavengers may be possible. Paleontologists believe that at least nine-tenths of the organic evolution into main stocks was accomplished before the Cambrian. The Cambrian record contains evidence for the existence of all phyla excepting the vertebrates, and the unsuccessful search for vertebrate fossils in the Cambrian cannot be regarded as conclusive evidence for their absence. The burden of proof, therefore, rests heavily on any theory based on

[1] C. Wyville Thomson, *Depths of the Sea,* 502–11.

[2] Philippi, *Neues Jahrb.* (1907), 444.

radical differences in the organic development of the early Paleozoic, as compared with the present, and a correlative, fundamental difference in the constitution of the ocean.

Nor would all students of the pre-Cambrian admit that the profound importance which Daly attaches to the post-Huronian erosion cycle is evident. It was preceded by at least three periods of emergence in the Lake Superior and Lake Huron regions and in Finland. So far as known, any one of them may have contributed as much lime to the sea as the post-Huronian.

Deposition of magnesian limestones by marine organisms.—Marine organisms deposit magnesium carbonates in small quantities. According to G. Forchhammer,[1] marine shells and corals contain magnesium carbonate in varying amounts from 0.15 to 7.64 per cent, 1 per cent being rather above the average. In *Lithothamnium nodosum*, Gümbel[2] found 2.66 per cent of magnesium and 47.14 per cent lime, and Högbom[3] in fourteen analyses of algae belonging to this genus reports from 1.95 to 13.19 per cent of magnesium carbonate.

The development of magnesium limestones and dolomites by marine leaching.—It has been shown that marine leaching is very effective in concentrating the magnesian content of limestone formations. This is due to the fact that calcium carbonate is several times as soluble as magnesium carbonate, as was first shown by Bischoff. The decrease in calcium carbonate and the corresponding increase in magnesium carbonate resulting from marine leaching is well shown in the table on p. 333, compiled by G. Högbom.[4]

Högbom[5] washed the clay marl of Upsula with carbonated water with the following results. The original composition of the marl was calcium carbonate, 18 per cent, magnesium carbonate, 1.3 per cent. The loss of calcium carbonate was about 50 per cent, while the loss of magnesium carbonate amounted to only a trace.

In his studies of the marine marls of Sweden, Högbom found that the transported material contained progressively larger proportions of magnesium as its distance from the parent limestone increased. Near its point of origin, the marl carried 3.7 parts of magnesium carbonate to 100 of calcium carbonate, and from these figures the ratio was generally raised to 36 magnesium carbonate and 100 calcium carbonate.

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[1] G. Forchhammer, *Neues Jahrb.* (1852), 854.

[2] Quoted from *Bull. 330, U.S.G.S.*, 485.

[3] Högbom, *Neues Jahrb.* I (1894), 262.

[4] *Ibid.*, 262–74.

[5] *Ibid.*, 268.

TABLE II

TABLE COMPUTED FROM 21 GLOBERGERINA, 21 RED MÜDS, 7 RADIOLARIAN OOZES, PTEROPOD OOZE, DIATOM OOZE, AND BLUE MUD

$CaCO_3$ Limits	$CaCO_3$	$MgCO_3$	Relative Values*	Analysis
80–100	86.7	17	.8	8
60–80	68.3	1.4	2.0	8
40–60	52.	1.2	2.4	8
20–40	32.	.9	3.0	3
10–20	16.2	1.6	10.0	4
5–10	6.1	.7	11.5	1
3–5	3.7	1.6	43.0	7
1–3	2.0	2.1	105.0	9

* Relative values express parts of $MgCO_3$: 100 parts of $CaCO_3$.

The stalactites from the caverns in the coral rocks of Bermuda, according to Högbom, contain only 0.18 to 0.68 per cent of magnesium carbonate, while the rocks themselves carry about five times as much magnesium carbonate. The lime salt has evidently dissolved much more freely than the magnesium compound. This mode of concentrating magnesium carbonate must, from the evidence cited, be regarded as real, and may be instrumental in causing the development of dolomite. It is obvious that the smaller the content of calcium in the sea, as compared with magnesium, that is, the smaller the relative quantity of calcium resulting from the difference between contribution from the land on the one hand, and precipitation on the other, the more effective will be the process of leaching. The precipitation of calcium carbonate in the sea is now largely controlled by life processes, and probably has been at least as far back as the beginning of the Paleozoic, so that since Zoic times there has been a powerful agency at work, tending to deplete the calcium content of the sea, while leaving the soluble magnesium salts to accumulate. Solid phases of calcium carbonate are therefore farther removed from a condition of equilibrium with sea water than the corresponding magnesium salt. Aside, then, from 'the inherent difference between the solubility of calcium carbonate and magnesium carbonate, the chemistry of the sea apparently facilitates the solution of calcium carbonate and retards that of magnesium carbonate. Assuming that the efficiency of the organic precipitation of calcium carbonate has been about the same throughout Zoic times, it seems obvious that the concentration of magnesium carbonate in calcareous deposits by marine leaching would have been even more effective than now, if at some time in the past the rivers had contributed relatively less lime and more magnesia than at present. If there is any probability that such has actually been the case, that would constitute one factor which would operate to cause an increase in the magnesium content of limestone in descending the geologic time scale.

The origin of dolomite by the secondary replacement of calcium by magnesium in the sea.—Coral rocks originally contain only a small percentage of magnesium carbonate, usually less than 1 per cent. In 1843, J. D. Dana[1] in a rock from the coral island of Makatea, in the Pacific, reported magnesium carbonate to the extent of 38.07 per cent. This approached the dolomite ratio which requires 45.7 per cent, and it was suggested that the rock had been dolomitized through secondary replacement, the magnesium carbonate probably having been derived from the concentration of shallow lagoons of sea water. Since Dana's time, many other investigators have recorded similar enrichments of coral reefs. In a coral reef from Porta do Mangue, Brazil, T. C. Branner[2] reports 6.95 per cent of magnesia, equivalent to 14.6 of carbonate, while the corals themselves contained only 0.20 to 0.99 per cent of magnesia. E. W. Skeats[3] reports analyses of dolomitic coral rock of the Pacific in which the magnesium carbonate rises to a maximum of 43.3 per cent.

The borings from the atoll of Funafuti as discussed by J. W. Judd[4] present a remarkable case of transformation from reef rock to dolomitic limestone. The principal boring was driven to a depth of 1,100 feet, through coral and coral rock all the way, and samples of the cores were analyzed every ten feet of the distance. The following table of data, quoted by *Bull. 330, U.S.G.S.*, p. 487, shows first, an enrichment in magnesium carbonate near the surface, then an irregular rising and falling in much smaller amounts, while below 700 feet the rock approaches the dolomite ratio.

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[1] J. D. Dana, *Corals and Coral Islands* (3d ed.), 393.

[2] T. C. Branner, *Bull. Mus. Comp. Zoöl.*, XLIV (1904), 264.

[3] E. W. Skeats, *Bull. Mus. Comp. Zoöl.*, XLII (1902), 53–126.

[4] J. W. Judd, *The Atoll of Funafuti*, quoted from *Bull. 330, U.S.G.S.*, 487.

TABLE III

MAGNESIUM CARBONATE IN BORINGS ON ATOLL OF FUNAFUTI

Depth Feet	Percentage $MgCO_3$	Depth Feet	Percentage Magnesium Carbonate
4	4.23	295	3.6
13	7.62	400	3.1
15	16.40	500	2.7
20	11.99	598	1.06
26	16.0	640	26.33
55	5.85	698	40.04
110	2.11	795	38.92
159	0.79	898	39.99
200	2.70	1000	40.56
250	4.9	1114	41.05

In the analyses of coral rock borings from an artesian well at Key West, Florida, reported by George Steiger,[1] there is no apparent relation between the content of magnesia and depth as shown by the borings on the atoll of Funafuti.

TABLE IV

LIME AND MAGNESIA IN BORINGS AT KEY WEST

Depth Feet	Percentage CaO	Percentage MgO	Depth Feet	Percentage CaO	Percentage MgO
25	54.03	0.29	1325	54.49	0.62
100	54.01	0.77	1400	55.12	0.30
150	54.38	0.86	1475	54.48	0.73
350	51.46	1.67	1625	53.90	1.14
600	48.87	2.50	1850	54.28	1.12
775	46.53	6.70	2000	54.02	1.06
1125	53.84	0.86			

The dolomitization of organic calcareous deposits in the sea by secondary replacement as well as by leaching seems to be too well established to admit of serious doubt. The degree of dolomitization in any given case may be influenced slightly by the original composition of the calcareous secretions: witness the difference in the content of magnesium carbonate in secretions from Lithothamnium and other members of this genus as compared with those of the corals. Certain calcareous secretions have been found to consist of calcite while others like those of the corals consist largely of aragonite. Aragonite is much less stable than calcite, hence the aragonite secretions are probably much more subject to dolomitization through leaching and replacement than the more stable form of calcium carbonate, calcite. Furthermore, it is highly probable that the composition of the sea is an important factor in dolomitization. If sea water is high in magnesium and low in calcium, it is probable that the conditions are more favorable for the dolomitization of calcareous deposits than if the reverse condition prevailed, as may be inferred from the following experiments. If a crystal of calcite is placed in water, solution will take place until equilibrium is reached between the calcite and the solution. Obviously, replacement, in the absence of magnesium salts, cannot take place. On the other hand, Sorby found that a crystal of calcite placed in a concentrated solution of magnesium chloride became slowly incrusted with magnesium carbonate, and Pfaff developed a dolomitic material by subjecting calcium carbonate to the action of a solution of magnesium chloride or sulphate and common salt, under pressure comparable to the deep sea, in which case the speed of reaction was proportional to the concentration of the solution.

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[1] George Steiger, *Bull. 228, U.S.G.S.* (1904), 309.

It is obvious that 60 pounds of calcium carbonate could not be replaced by a solution containing only 10 pounds of magnesium salt in anything like the proportions required by the dolomite ratio. It seems equally probable, a priori, that if the river waters carried calcium and magnesium to the sea in the ratio of 1:1, the chances for dolomitization through leaching, secondary replacement, or possibly primary deposition would be better, all other things being equal, than when the proportion of river-borne calcium to magnesium is 6:1, which is the approximate ratio at the present time according to the best estimate.[1]

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[1] See F. W. Clarke, "A Preliminary Study of Chemical Denudation," *Smithsonian Mis. Coll.*, LVI, No. 5, p. 8.

Experimental evidence on the origin of dolomite by secondary replacement of calcium chloride.—A summary of the principal experimental methods by which the dolomitization of calcium carbonate by replacement has been effected follows:

1. REPLACEMENT AT HIGH TEMPERATURE

By heating calcium carbonate and a solution of magnesium sulphate in a closed tube at 200° C. (Morlot, *Jahresb. Chemie* [1847–48], 1290).

By heating carbonate of lime to over 100° C. with a solution of magnesium bicarbonate (F. Hoppe-Seyler, *Zeitsch. Deutsch. Geol. Gesell.*, XXVII [1875], 509).

By the action of a solution of magnesium chloride on calcium carbonate at high temperature (Marignac and Faber, *Compt. Rend.*, XXVIII [1849], 364).

By saturating chalk with a solution of magnesium chloride and heating the mass on a sand bath (Saint-Claire Deville, *Compt. Rend.*, XLVII [1858], 91).

By heating fragments of porous limestone with dry magnesium chloride in a gun barrel (J. Durocher, *Compt. Rend.*, XXXIII [1851], 64).

It is probable that the preceding experiments on the replacement of calcium carbonate have very little significance in relation to the development of dolomite in the sea, since the continuity of the life record back as far as the pre-Cambrian, at least, precludes the possibility of a universally hot ocean. Very locally, as in the case of the eruption of Krakatao, the required temperatures may have been duplicated in the ocean. They are more likely to have been paralleled in some cases of contact, metamorphism of limestones generally following their emergence from the sea.

2. REPLACEMENT ABOVE 60° C.

By action of magnesium sulphate on aragonite in a concentrated solution of common salt at a temperature above 60° C. (Klement, *Min. Pet. Mitth.*, XIV [1894], 526).

The same objection holds against the application of this experiment of the development of dolomite in the sea as was urged against the preceding group of experiments. The highest temperatures of the sea, resulting from solar heating, on record are those of the Red Sea[1] (31° C.), and the Lagoons of the Celebes (32° C.).

3. FORMATION OF DOLOMITE AT ORDINARY TEMPERATURE AND PRESSURE

By action of magnesium chloride and magnesium sulphate in water on anhydrite in the presence of common salt and carbonic acid (Pfaff, Jr., *ibid.*, 557).

By action of hydrogen sulphide in water on magnesium and calcium carbonates, followed by the introduction of carbonic acid (Pfaff, Jr., *ibid.*, 556).

4. FORMATION OF DOLOMITE AT ORDINARY TEMPERATURE AND HIGH PRESSURE

By the action of sodium carbonate on anhydrite in the presence of common salt in a concentrated solution of magnesium sulphate or chloride (Pfaff, *ibid.*, 562).

By the action of magnesium chloride or sulphate in a solution of common salt on calcium carbonate. The speed of the reaction is proportional to the degree of concentration of the solution (Pfaff, *ibid.*, 565).

Pfaff's experiments are highly creditable in that the replacement of calcium carbonate by a magnesium salt so as to yield a product approaching the dolomite ratio was effected without resort to high temperatures. Doubtless other methods will yet be worked out whereby this result can be obtained under conditions similar to those prevailing in the sea. The last experiment by Pfaff is highly suggestive when compared with the increase in the magnesium content of marine oozes with depth; that is with pressure (see this paper, p. 335). However, it does not seem safe to argue that this has been a very important factor of control, since many dolomites have very obvious earmarks of shallow-water deposition, such as ripple marks, cross-bedding, and interstratification with coarse sands.

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[1] Quoted by F. W. Pfaff, *Neues Jahrb. Min. Beilage*, XXIII (1907), 573.

B. THE EVIDENCES FOR THE ORIGIN OF DOLOMITE BY THE METAMORPHISM OF LIMESTONES AFTER THEIR EMERGENCE FROM THE SEA

Direct chemical precipitation of dolomite.—The occurrence of dolomite in veins and vugs of limestone and dolomite is well known. So far as the recorded facts seem to indicate, direct chemical precipitation of dolomite in fissures and openings of carbonate formations, after emergence from the sea, seems to be much more important than the chemical precipitation of dolomite in the sea at the present time. However, dolomite as a cement and vein filler is quantitatively of far less consequence than calcite. Furthermore, it is not certain to what extent dolomite in veins merely means the transfer of previous existing dolomite originally developed in the sea. Direct chemical precipitation of dolomite in formations after their emergence from the sea, while probably more important than the chemical precipitation of dolomite in the sea at the present time, is nevertheless a very subordinate process and cannot be regarded as an important source of dolomite formations.

Origin of dolomite by leaching limestones after their emergence from the sea.—The dolomitization of limestones after their emergence through leaching is a very important process wherever both the calcium carbonate and dolomite are originally present, because of the differential solubility of the two carbonates. Unquestionably a unit volume of water as it enters the soil, but charged with atmospheric gases, is a much more efficacious solvent than an equal volume of sea water, but the total volume of sea water which is effective in leaching carbonates in the sea is vastly greater than the volume of water in the lithosphere. Leaching of limestones by underground waters probably changes the ratio of calcium to magnesium but little excepting near the surface, because the porosity, slumping, and faulting which would need to follow from converting a magnesian limestone containing even 13 per cent of magnesium carbonate into a dolomite through leaching is not at all evident in dolomite formations. Evidence is cited showing that weathering does increase the percentage of magnesia in limestones. Since effective leaching of limestones by ground water is related to weathering, it is improbable that this process accounts for the stratigraphic separation of limestones, magnesian limestones, and dolomites, or for any large proportion of the dolomite in nature.

Origin of dolomite by secondary replacement of limestone.—Secondary dolomitization along fissures had been described by Prestwich,[1] Geikie,[2] Bain,[3] Pfaff,[4] Spurr,[5] and others. The alteration of limestones by hot, magnesian spring waters at Aspen, Colorado, described by Spurr is significant, but obviously, secondary replacement by underground water seems to be only local. A brief consideration of the chemistry of ground water and of the ocean is suggestive in showing the probabilities for the relative replacing power of sea water and underground water. Sea water[5] contains calcium and magnesium in the ratio of 1 to 3.11. The salinity is 3.301 to 3.737, of which 1.197 per cent is calcium and 3.725 per cent magnesium. The constitution of underground water is variable and depends upon the local composition of the rocks from which it is taken. Underground water of terrestrial origin is nearly free from mineral matter at the start but contains solvent gases from the atmosphere. Obviously, if a unit volume of unmineralized underground water comes into contact with a unit weight of carbonate rock, solution follows until equilibrium is attained between the solid and liquid phases which are in contact. If the temperature, pressure, and the volume of water remain unchanged nothing further results. It is this history of the source of the salts in terrestrial underground waters which is unfavorable to replacement.

In humid regions, underground waters are essentially carbonate waters in which the principal positive ion is calcium. The following analysis may be taken as illustrative:

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[1] Prestwich, *Geology—Chemical, Physical and Stratigraphical* (Oxford, 1886), I, 133–44.

[2] Geikie, *Textbook of Geology* (3d ed.; MacMillan, London, 1893), 321.

[3] Bain, "Preliminary Report on the Lead and Zinc Deposits of the Ozark Regions," *Twenty-second Ann. Rept. U.S. Geol. Survey*, Part II (1901), 208–10.

[4] Pfaff, *op. cit.*, XXIII (1907), 529–80.

[5] Spurr, "Geology of the Aspen Mining Dist., Colorado," *Mon. U.S. Geol. Survey*, XXXI (1898), 210–91.

[5] Mean of 77 analyses of ocean water from many localities collected by the Challenger expedition. Quoted from *Bull. 330, U.S. Geol. Survey*, 94.

COMPOSITION OF EXCELSIOR SPRINGS, MISSOURI[1]

SALINITY 489 PARTS PER MILLION OF WATER, OR ABOUT 0.4 PER CENT

Ca	29.28
Mg	3.15
Co_3	55.92

Ratio of Ca to Mg 9.3:1

The calcium carbonate of the ocean bottom is in contact with a solution high in magnesium and low in calcium, largely derived from the lands and not from the ocean bottom. The calcium carbonate of the land areas is on the average, so far as humid climates are concerned, in contact with carbonated waters high in calcium and low in magnesium whose salts are derived from the decomposition of the rocks through which they circulate. In the light of experimental evidence, on the replacement of calcium carbonate by magnesium carbonate, where are the conditions more favorable for dolomitization by replacement, in the ocean or in the sea of underground water? Of course there are analyses of underground waters which show a high content of magnesium, which could possibly cause dolomitization, but these seem to be either exceptional or local.

C. EVOLUTION VERSUS THE METAMORPHISM OF LIMESTONES AFTER THEIR EMERGENCE FROM THE SEA AS EXPLANATION FOR THE INCREASE IN THE RATIO OF CALCIUM TO MAGNESIUM OF LIMESTONES AND DOLOMITES WITH GEOLOGIC TIME

Evidence has been presented for both the development of dolomite in the sea and its origin by the metamorphism of limestones after their emergence from the sea. Magnesian limestones can develop in the sea from a combination of organic and inorganic processes. The known inorganic processes are direct chemical precipitation, leaching, and secondary replacement. These may also be effected through the agency of underground water. Evidence has been presented to show that these processes are operative in the sea on a much larger and more uniform scale because of the chemical properties of the sea as compared with those of underground water. Underground waters derive their dissolved materials from the rocks through which they circulate, and generally are high in calcium and low in magnesium, whereas the sea derives its materials largely from the lands and not from the ocean bottom. Sea water is low in calcium and high in magnesium, and is therefore a more favorable as well as a more universal medium for effecting the dolomitization of the ocean bottom than is underground water for the dolomitization of the rocks through which it circulates. The direct evidence for the dolomitization of limestones by underground waters which has been presented shows only local dolomitization along fissures and other openings, principally in the belt of weathering or in localities permeated by waters of unique chemical compositions, such as hot magnesian springs. The occurrence of dolomites of vast thickness and extent and the interstratification of limestones and dolomites cannot therefore find a ready explanation in the mutative agency of underground waters. Excepting for certain local occurrences, dolomite formations seem to have developed in the sea, rather than by the metamorphism of limestones after their emergence from the sea. The evolution of dolomite and limestones through a decline in the deposition of dolomite with time, therefore, seems to have a high degree of probability. Consequently, the gradual alternation from the predominance of dolomite in the ancient sediments to the dominance of limestones of a high ratio of calcium to magnesium in more recent times has probably been due to gradual changes in the condition of deposition in the sea.

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[1] From *Bull. 330, U.S. Geol. Survey,* 150.

WHAT FACTORS CONTROLLING THE DEPOSITION OF CALCAREOUS MARINE DEPOSITS HAVE UNDERGONE A GRADUAL EVOLUTION RESULTING IN THE EVOLUTION OF THE LIMESTONES AND DOLOMITES?

Four factors directly control the composition of the materials precipitated on the ocean floor: namely, pressure, temperature, life processes, and the chemical composition of the sea. Which of these factors has undergone a progressive change, reflected in the evolution of limestone and dolomites? It is almost needless to consider whether the pressures on the ocean floor have undergone a progressive evolutionary change within geologic time. All the water-deposited sediments found on the continents appear to have the character of deposits now forming in shallow or moderate depths. None are like the abysmal deposits of the present ocean, a forceful argument for the permanence of the continents and the oceans. Nor is there any probability that the temperature of the ocean has undergone a progressive change which would account for the evolution of limestones and dolomites. The continuity of the life record down to the base of the Cambrian precludes the possibility of any marked change in the temperature of the ocean throughout Zoic times. But even beyond the Cambrian this relative uniformity of temperature may have persisted for a period of time, as long or even longer than from the Cambrian to the present, for paleontologists believe that approximately nine-tenths of the evolution of life into main stocks was completed at the beginning of the Cambrian. All the phyla are represented in the Cambrian excepting the vertebrates, and the fact that no vertebrate fossils have been found in the Cambrian cannot be regarded as positive proof that even they did not exist at this remote period of earth history. On the other hand, more and more evidence is accumulating in favor of Chamberlin's philosophic conception that the temperature of the ocean and the climatic conditions of the continents have undergone oscillations in consequence of periodic, areal changes of the lands with respect to the sea; that periods of land expansion are characterized by zonal, diversified climates, tending toward world-wide aridity and refrigeration, while periods of maximum oceanic expansion are associated with climatic uniformity, moderation, and humidity. There is then no probability that the temperatures of the ocean have undergone an evolution consonant with the evolution of dolomite and limestone.

Could the evolution of living organisms have been the controlling factor in the evolution of limestones and dolomites?

It would be difficult to disprove that organic control was a factor in the problem. Organisms play a gigantic rôle in the distribution of lime at the present time, and have for ages past. Biologists, however, lend considerable support to the hypothesis that organic activities are adaptations to physical and chemical environment, rather than creators of environment. In the long run, they may cause profound changes in environment, but the keynote of their activity is adaptation rather than control. The selection of potassa rather than soda by the land plants and the selection of soda in preference to potassa by marine plants has been cited as evidence for the adaptation of life processes to chemical environment. The preference of lime-secreting organisms for calcium rather than for magnesium may be a similar adaptation. It is suggestive that calcium carbonate is the principal salt contributed to the sea, and that in localities most favorable to life, lime carbonate is the most insoluble of the important salts of the sea. Recent biological studies have also shown that magnesium salts are to a certain extent deleterious to life processes. While the relation of life processes to environment is problematical, the evidence favors the physical control of life processes, rather than the control of environment by life processes.

Even if the immediate control of the evolution of carbonate rocks was largely by organic agencies, the causation of the control may logically be looked for in the environment. The change in the calcium magnesium ratio, which characterizes the evolution of the carbonate rocks, suggests under this hypothesis that it is related to a similar change in the calcium magnesium ratio of the materials contributed to the sea. It has been indicated already that waters containing a high proportion of magnesium to calcium are more efficient in causing the development of dolomite than those which do not. The salts of the sea are inherited from the metamorphic processes which have worked the earth over and over again. The circulation of the rock materials from one environment to another involves adaptations. The materials adapted to the new conditions tend to be stable. Others undergo conversion to new mineral forms. Some, finding no place in the new environment, are expelled and may finally reach the sea, where they again undergo environmental adaptations. Could it be possible that the ratio of river-borne calcium to magnesium, which is now approximately 6 to 1, has undergone an evolution throughout geologic times marked by a gradual increase in calcium and decrease in magnesium? A progressive change in the proportions of calcium and magnesium contributed to the sea might have been consummated either by a progressive change in the agents and processes of metamorphism and sedimentation or by a progressive change in the calcium and magnesium content of the lands. It cannot very well be assumed that the nature of the agents and processes which contribute calcium and magnesium to the sea has undergone any marked change during geologic time. The continuity of the life record, the uniformity of sedimentation, and the duplication of climatic conditions down to the remote past speak against it. How then could the constitution of the lands, apparently the only remaining alternative, undergo a progressive change which in turn caused a progressive increase in the ratio of calcium and magnesium contributed to the sea, under uniformitarian processes? The answer to this problem is sought in the nature of the redistribution of calcium and magnesium in consequence of metamorphic and depositional processes.

[*To be continued*]